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V.

A METHOD FOR THE SEPARATION AND ESTIMATION OF BORIC ACID,

WITH AN ACCOUNT OF A CONVENIENT FORM OF APPARATUS FOR QUANTITATIVE DISTILLATIONS.

By F. A. Gooch.

Presented June 16, 1886.

In all successful methods for the estimation of boric acid, its comparative isolation is a necessary preliminary. Fortunately the removal of nearly everything which interferes seriously with the proper execution of methods is not particularly arduous, but, of ordinarily occurring substances, two, silica and alumina, — both very commonly associated with boric acid, — are especially annoying in this regard. In the separation of alumina the trouble lies in the tendency of the precipitated hydrate to carry and retain boric acid,* so that the two cannot be parted by means of ammonia or ammonia salts; with silica, the difficulty is in removing it completely. The volatility of boric acid stands, of course, absolutely in the way of treating with acid and evaporating to dryness, and every chemist knows the vainness of attempting to precipitate silica by means of ammonia, ammonia salts, or zinc oxide in ammonia. In Stromeyer's method † the presence of silica is peculiarly harmful, since in passing to the condition of potassium fluosilicate this substance nearly quadruples its weight, and to free the potassium fluo-borate from contaminating fluo-silicate requires, according to Fresenius,‡ at least six treatments by solution in boiling water, the addition of ammonia, and evaporation to dryness. Wöhler § recommends evaporating the hydrochloric acid solution to dryness in a flask fitted to a condenser, collecting the distillate, reuniting the latter with the residue, and filtering from silica; and the operation is successful so far as the complete removal of silica is concerned, but the alumina, if present, is still in condition to give annoyance, and the other bases are yet to be separated.

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* Wöhler, Ann. d. Chem. u. Pharm., cxli. 268.

† Ann. d. Chem. u. Pharm., c. 82.

‡ Quant. Chem. Anal., p. 424.

§ Handbook of Mineral Analysis, under Datholite.

Advantage has long been taken of the volatility of free boric acid with hydrofluoric acid or with alcohol to secure its removal from fixed substances, but so far as I know no attempt has been made heretofore to secure its complete volatilization and estimation in the distillate. The experiments which I proceed to describe are the result of an effort to accomplish this end.

Aside from the difficulties in manipulation and in the construction of apparatus which the use of hydrofluoric acid would involve, this reagent is otherwise plainly inapplicable to the purpose in view, and of other agents with which boric acid is known to volatize freely methyl alcohol seems to present the most desirable qualities. Methyl alcohol, ethyl alcohol, and water are effective in the order in which they are named. Thus, to volatilize 1 grm. of boric acid, — the equivalent, speaking roughly, of about 0.5 grm. of boric anhydride, — two treatments with 10 cm.^{3} of methyl alcohol and evaporation to dryness in each case were adequate; for the volatilization of 0.2 grm. of boric acid were required two treatments of 10 cm.^{3} each of ethyl alcohol, succeeding an evaporation with 50 cm.^{3} of the same alcohol; and the residue of five evaporations of water over 0.4 grm. of boric acid, taking in each case 50 cm.^{3} of water, followed by ignition, weighed 0.08 grm., or one fifth of the original weight. In the presence of water, methyl alcohol is not equally effective; amyl alcohol and sulphuric acid restrain its action similarly, doubtless by dilution simply, and hydrochloric acid seems to possess no advantage over water alone in developing the volatility of boric acid. As an example, an experiment may serve in which a solution of 0.4 grm. of boric acid in 50 cm.^{3} of water, after being heated three times successively with 25 cm.^{3} of methyl alcohol until the boiling point rose in every case nearly to that of water, and then evaporated to dryness, left a large residue which disappeared with a single charge of 25 cm.^{3} of methyl alcohol applied by itself.

From the residue of the evaporation of borax with hydrochloric, nitric, or acetic acid, methyl alcohol, as would naturally be predicted, volatilizes the boric acid freely, though the presence of foreign material acts to a certain degree protectively and tends to diminish the rapidity with which the alcohol would otherwise effect extraction and volatilization. In case, however, that acetic acid is used to break up the borate, the tendency of sodic acetate to lose acid and become alkaline simply by exposure to evaporation in its aqueous solution makes it necessary to insure the acidity of the residue of evaporation by adding a drop or two of acetic acid before repeating the treatment with methyl alcohol.

On the whole, methyl alcohol shows itself to be an excellent agent by which to secure the volatilization of boric acid.

To retain free boric acid, magnesium oxide naturally suggests itself. According to Marignac* it is effective, and, if in the course of analysis it may have been partly converted to the chloride, it is easily regenerated by the action of heat and moisture. Marignac, it will be remembered, makes use of magnesia mixture — the chlorides of ammonium and magnesium with free ammonia — to fix the boric acid, evaporating the solution to dryness, igniting, extracting with boiling water, filtering, and weighing the residue, while the filtrate is again treated as before to recover traces of the borate which have yielded to the solvent action of the water. During the drying and ignition the magnesium chloride yields hydrochloric acid, and it would seem scarcely possible that the magnesium borate should fail to show some loss of boric acid when both hydrochloric acid and moisture exert their action. Further, the presence of ammonia during evaporation does not prevent the volatilization of boric acid,† and Marignac regards the addition of it from time to time as of doubtful use. So it appears natural to look for some loss under such conditions, and Marignac fully recognizes the fact that the apparent accuracy of his method is due to the balancing of errors, the inclusion of foreign matter by the magnesium borate and the deficiency of the magnesia when precipitated as ammonio-magnesium phosphate together compensating for the loss of boric acid by volatilization. To bring the matter to the test, the following experiments were made. In them and in all succeeding experiments the boric acid was weighed in solution, the standard of this having been fixed by dissolving in a known weight of water a known weight of fused boric anhydride prepared in a state of purity by frequent recrystallization. The magnesium oxide employed was made from the pure chloride by precipitating by ammonium carbonate and igniting, and was free from lime and alkalies, and as far as could be determined otherwise pure. The whole operation of each experiment was conducted in one vessel, so as to avoid transfers. In all cases a weighed platinum crucible of 100 $cm.^3$ capacity received a weighed portion of magnesia, and after ignition and subsequent weighing the weighed solution of boric acid was introduced. In experiments (1) to

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* Zeit. für Anal. Chem., i. 406.

† Rose, Pogg. Ann., lxxx. 262.

(4) the magnesia was thoroughly stirred in the solution of boric acid, the evaporation carried at once to dryness, and the crucible and residue ignited and weighed; in experiments (5) to (8), the magnesia was dissolved, after the addition of the boric acid, in hydrochloric acid sufficient in amount to prevent the precipitation of magnesium hydrate on the subsequent addition of ammonia, ammonia introduced in considerable excess in (7) and (8), in distinct excess in (5) and (6), the whole evaporated and ignited, the residue moistened and again ignited, and this last treatment repeated until the residue ceased to yield vapor of hydrochloric acid when heated.

	B_2O_3 taken.	MgO taken.	$MgO+B_2O_3$ found.	B_2O_3 found.	Error.
	grm.	grm.	grm.	grm.	grm.
(1)	0.1734	0.5005	0.6607	0.1602	0.0132—
(2)	0.1804	0.4973	0.6660	0.1687	0.0117—
(3)	0.1793	0.4949	0.6640	0.1691	0.0102—
(4)	0.1794	0.4941	0.6627	0.1686	0.0108—
(5)	0.1807	0.4984	0.6542	0.1558	0.0249—
(6)	0.1789	0.4974	0.6687	0.1560	0.0229—
(7)	0.1806	0.4944	0.6684	0.1740	0.0066—
(8)	0.1789	0.4959	0.6672	0.1713	0.0076—

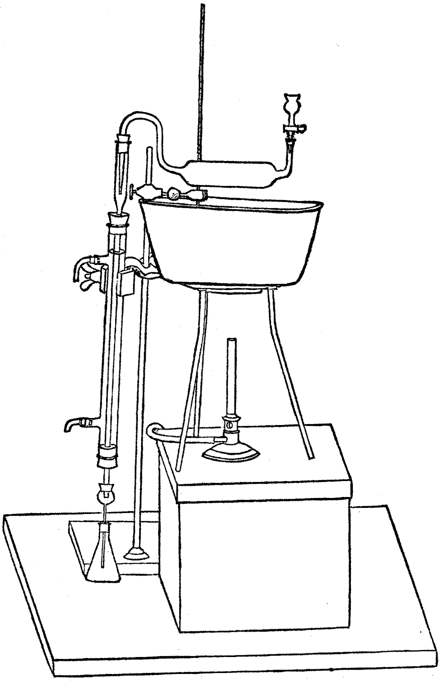
From these results it appears plain that under the conditions of the experiments neither magnesia alone nor the magnesia mixture is efficient in fixing boric acid; but in experiments (7) and (8), in which ammonia was employed in large excess, the loss of boric acid is least, so that it would seem to be the case that though ammonia is not a perfect preventive of volatilization it does exert a restraining action on the boric acid. That the magnesia mixture should be incapable of retaining entirely the boric acid present is, as has been pointed out, not surprising; but that the loss should be so great is rather startling, and more than suggests that the errors of Marignac's process are seriously excessive. The failure of magnesium oxide to hold back boric acid under the conditions of the experiment must be due to a cause other than that which determines the loss during the evaporation and ignition of the magnesia mixture, and for this it is natural to turn to the insolubility of the oxide, — a quality likely to oppose some difficulty in the way of establishing complete contact between the boric acid and the magnesia during a short exposure. Direct tests of this point showed distinctly that mixtures of boric acid in water and magnesia, when submitted at once to distillation, yielded boric acid to the distillate; but that, if the mixtures were permitted to stand some hours before distilling, the oxide passed to the semi-gelatinous condition of the hydrate, and retained the boric acid so firmly that turmeric failed to show the presence of the latter in the distillate. It is plain, therefore, that with sufficient preliminary exposure magnesia might be relied upon to retain boric acid; but inasmuch as long and perhaps somewhat indefinite periods of waiting are objectionable in any analytical process, it was thought best to try the effect of substituting lime for magnesia. Experiments (9) to (12), conducted like the previous ones, excepting only the use of carefully prepared and ignited calcium oxide instead of magnesium oxide, were made with this end in view.

	B_2O_3 taken.	CaO taken.	$CaO+B_3O_3$ found.	B_2O found.	Error.
	grm.	grm.	grm.	grm.	grm.
(9)	0.1810	0.9737	1.1560	0.1823	0.0013+
(10)	0.1819	0.9750	1.1583	0.1833	0.0014+
(11)	0.1808	0.9922	1.1810	0.1818	0.0010+
(12)	0.1833	0.9715	1.1560	0.1845	0.0012+

These figures indicate sufficiently that there is no loss of boric acid by volatilization when its aqueous solution is evaporated in contact with calcium hydrate; but, inasmuch as the comparative solubility of the latter is the quality which makes it effective where magnesia is not, it seemed desirable to test the action of calcium hydrate in alcoholic solutions, in which it is very insoluble. The experiment showed that when the solution of boric acid in methyl or ethyl alcohol is put upon lime and distilled at once loss is apt to take place, and sometimes to a very inconsiderable amount, but that a short period of digestion with occasional stirring — from five to fifteen minutes — is sufficient to obviate danger of volatilization of boric acid.

It appears, therefore, that, free boric acid being easily volatilized by means of methyl alcohol and fixed completely by calcic hydrate, the separation of the acid from almost everything with which it occurs ordinarily and its estimation subsequently depend only upon the practicability of distilling it from its compounds in such company that it may be retained by lime and its amount determined by the increase in the weight of the latter. Unlike magnesium chloride, calcium chloride does not yield its chlorine readily under the action of heat and moisture naturally retained; so that hydrochloric acid must not be present with boric acid which is to be estimated in the manner described. Calcium nitrate and calcium acetate both yield the oxide without difficulty upon ignition, and nitric and acetic acids are suitable agents, therefore, for the liberation of boric acid previous to distillation.

The actual distillation presented at first some difficulty, — for the repeated, thorough, and rapid evaporation of a liquid charged with soluble or insoluble solid matter is apt to involve some mechanical transfer to the distillate of material which should remain in the residue, — but the device of the following description solves the problem successfully.



The apparatus, which is shown in the accompanying cut, consists essentially of a retort, condenser, and bath for heating. For the last I have used a paraffine bath, as being on the whole the most convenient. The condenser is set vertically, to facilitate changing the level of the retort within the bath, and to secure at the same time continual and thorough washing of the tube by its own condensations. The retort, somewhat like the well-known drying tube of Liebig in general shape, is easily made of a pipette by bending the tube at one end to a right angle, at the other to a goose-neck, as shown. To the former end is fitted, by a rubber stopper or section of tubing, a glass funnel-tube provided with a stop-cock; the end of the goose-neck passes tightly through a rubber stopper in the upper end of the condensing tube. This is essentially the apparatus, but it is convenient to attach to receive the distillate a small Erlenmeyer flask which moves with the condenser and is joined to it, in the manner indicated in the figure, by means of a thistle-tube and a rubber stopper grooved to permit the free passage of air. In carrying out a distillation, the liquid to be distilled is introduced into the retort either by the funnel tube or previous to its insertion, the glass cock is closed, the water started through the condenser, and the retort lowered into the hot paraffine, care being taken to begin the operation with the retort not more than half full and so inclined that only the rear dips below the surface of the bath. If the precaution to heat the retort at the start in this manner be overlooked, it may sometimes happen that the sudden and violent expulsion of air through the liquid will carry portions of it bodily into the goose-neck, and even into the condenser. With this point considered, the remainder of the operation presents no difficulty, and requires little care.

The size of the retort may be suited, of course, to the particular case in hand, but for most purposes a 200 cm.^{3} pipette makes a retort of convenient dimensions, neither too large for the distillation of small charges nor too small to permit the treatment of 100 cm.^{3} of liquid comfortably. The tube of the goose-neck should be wide enough to prevent the formation of bubbles in it; 0.7 cm. is a good measure for the interior diameter. It is of advantage to heat the bath to a point considerably above the temperature at which the liquid which is to be distilled boils, — something between 130° C. and 140° C. does very well for water, and is not too high for methyl alcohol, — and under such circumstances, and when the retort is entirely submerged, it often happens that evaporation takes place with extreme rapidity from the surface of the liquid in perfect quiet without actual boiling.

With such an apparatus the following experiments were made. The boric acid was weighed, as before, in solution, and to bring the condition of the experiment to that of an actual analysis, 1 grm. of pure sodium hydrate was added in solution, nitric acid or acetic acid to acidity and a little more, and the whole was introduced into the retort and distilled to dryness.

In those experiments in which nitric acid was employed, the methyl alcohol was introduced upon the residue thus dried in six successive portions of 10 cm.^{3} each, and distilled to dryness; but in order to break up the residue of sodium nitrate, which by its insolubility might effect to some extent the protection of the boric acid from the action of the alcohol, 2 cm.^{3} of water were introduced and evaporated between the second and third, and again between the fourth and fifth distillations.

When acetic acid was made use of to free the boric acid, the six distillations with methyl alcohol were made as before; but, sodium acetate being soluble in methyl alcohol, the intermediate treatments with water were unnecessary. With the fourth portion of methyl alcohol a few drops of acetic acid were added to preserve the acidity of the residue, which, as has been pointed out, tends to become alkaline under the treatment.

The residues of both processes of treatment were found to be free from boric acid by the exceedingly delicate test with turmeric, care being taken in the series of experiments in which nitric acid was used to oxidize nitrites by means of bromine (expelling the latter before making the test), and in the acetic acid series to acidify with hydrochloric acid sufficiently to counteract the tendency of the acetate by itself to brown the turmeric on evaporation.

The lime to retain the boric acid in the distillate was ignited in the crucible in which the evaporation of the distillate was to be made subsequently, and then transferred to the receiving flask attached to the condenser, so that the boric acid might be fixed during the distillation. To prevent the caking of the lime by the action of the alcohol, it was slaked with a little water before the distillation was begun.

In experiments (13) to (16) nitric acid was employed, and in (17) to (20) acetic acid was used, with the precaution noted, to liberate the boric acid.

	B_2O_3 taken.	CaO taken.	B_2O_3+CaO found.	B_2O_3 found.	Error.
	grm.	grm.	grm.	grm.	grm.
(13)	0.1738	0.9647	1.1392	0.1745	0.0007+
(14)	0.1806	0.9639	1.1456	0.1817	0.0011+
(15)	0.1779	0.9665	1.1450	0.1785	0.0006+
(16)	0.1824	0.9739	1.1587	0.1848	0.0024+
(17)	0.1806	1.4559	1.6371	0.1812	0.0006+
(18)	0.1812	0.9720	1.1543	0.1823	0.0011+
(19)	0.1788	0.9986	1.1781	0.1795	0.0007+
(20)	0.1813	0.9527	1.1358	0.1831	0.0018+

In experiments (13) to (16) the mean error amounts to 0.0012+ grm.; in experiments (17) to (18) the mean error is a little more than 0.0010+ grm. Throughout the entire series of experiments the tendency to yield figures slightly larger than the truth is manifest, but the error is quite within legitimate limits. The greatest care was taken to secure similarity of conditions under which the crucible and lime were weighed before and after the evaporation and absorption of boric acid, and the weight after ignition was taken in every case after cooling over sulphuric acid during a definite period of ten minutes in order to eliminate as far as possible the effect of atmospheric condensation upon the large surface of platinum. Ignitions were always finished over the blast-lamp, and constancy of weights secured.

The results of both modes of treatment are on the whole satisfactory, and equally so.

In the presence of chlorides, it is of course impossible to employ nitric acid to free the boric acid. Oxalic, citric, and tartaric acids also liberate hydrochloric acid to a considerable extent from alkaline chlorides. It was found, however, that when acetic acid was distilled over sodium and potassium chlorides only traces of hydrochloric acid passed into the distillate, and experiments (21) to (23) were made to determine whether these amounts are sufficient to vitiate the separation of boric acid from alkaline chlorides by distillation in presence of free acetic acid. The details of treatment were identical with those of experiments (17) to (20), excepting only the addition of 0.5 grm. of sodium chloride to each portion before distillation.

	B_2O_3 taken.	CaO taken.	B_2O_3+CaO found.	B_2O_3 found.	Error.
	grm.	grm.	grm.	grm.	grm.
(21)	0.1834	0.9842	1.1675	0.1833	0.0001—
(22)	0.1831	0.9755	1.1593	0.1838	0.0007+
(23)	0.1761	0.9740	1.1523	0.1783	0.0022+

The mean error of these results is about 0.0009+ grm., and it is plain that the presence of sodium chloride does not materially change the conditions of the experiment. There seems, therefore, to be no reason why boric acid may not be separated by distillation from alkaline chlorides in presence of free acetic acid; but it was found that the presence of any considerable amount of potassium acetate is disadvantageous. Sodium acetate to a reasonable amount does not interfere with the favorable progress of the separation; but potassium acetate appears to require a much higher temperature for the expulsion of its water, and longer distillation.

When, therefore, chlorides are present in the salts from which boric acid is to be removed by distillation, the choice is open between two methods: the distillation may be made directly with an excess of acetic acid; or the hydrochloric acid may be first removed by means of silver nitrate, and the distillation of the filtrate proceeded with at once, or after precipitation of the excess of silver salt by means of sodium hydrate or carbonate, care being taken to acidify again sufficiently with nitric acid after the removal of the silver. Of these two modes of proceeding, I incline to the treatment with nitric acid and the removal of the chlorine by precipitation; and this method has been used with success by others as well as myself, for some months, in the analysis of waters carrying boric acid, and natural borates.

The process in either modification is fairly accurate and easily executed, and admits of very wide application. Insoluble compounds in which the boric acid is to be determined may be dissolved in nitric acid at once, or, if necessary, first fused with sodium carbonate; and, fortunately, nearly everything which is volatile in the subsequent treatment and capable of forming with lime compounds not easily decomposable by heat may be removed by known processes. The combination of fluorine, silica, and boric acid is perhaps most difficult to treat; but the precipitation and removal of the first as calcium fluoride from the aqueous solution of a fusion in alkaline carbonate may, it is believed, be effected with care, and the mode of procedure from that point is simple.

The number of distillations necessary depends, of course, upon the amount of boric acid treated. To remove 0.2 grm. of boric anhydride completely to the distillate, six charges of methyl alcohol, of 10 $cm.^3$ each, proved, as we have seen, to be ample.

The apparatus by the aid of which the distillation processes which have been described were carried out has found useful application in a number of other processes. In the determination of free and albuminoid ammonia in waters which can be boiled quietly with difficulty, in the methods of estimating hydrofluoric acid which involve the expulsion of silicon fluoride from a mixture of the fluoride with sulphuric acid and silica, in the separation of iodine from bromides and chlorides by distilling with ferric sulphate and sulphuric acid, and of bromine from chlorides by means of permanganic acid, it has proved of value, and will doubtless be found convenient in many analytical processes in which quantitative separations by the distillation of liquids liable to spatter or boil explosively are involved.